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- (71) Applicant (for all designated States except US): **HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düsseldorf (DE).**
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SCHOENFELD, Rainer [DE/US]; 2136 S. Sanctuary Drive, New Berlin, WI 53151 (US). HUBERT, James, F. [US/US]; 21615 Holly Crest Drive, Brookfield, WI 53045 (US). ERMAN, Murteza [TR/US]; 2247 S. Sanctuary Drive, New Berlin, WI 53151 (US).**
- (74) Agent: **HARPER, Stephen, D.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).**
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**WO 03/078163 A1**

(54) Title: **EPOXY ADHESIVE HAVING IMPROVED IMPACT RESISTANCE**

(57) Abstract: In the preparation of an improved adhesive composition, an epoxy-based prepolymer is obtained by the reaction of one or more epoxy resins with amino-terminated polyethers and/or carboxyl-terminated butadiene-nitrile rubbers. In one embodiment of the invention, both a solid epoxy resin and a liquid epoxy resin, each of which is a diglycidyl ether of a polyphenol such as bisphenol A, are used. The epoxy-based prepolymer is mixed with an acrylate-terminated urethane resin (preferably, one based on a polyol having a number average molecular weight of at least about 400) and a heat-activated latent curing agent to make an adhesive composition which can be pumpable at room temperature. Curable adhesives capable of expansion to about 100% with high impact resistance after curing may be obtained by inclusion of expanding agents such as expandable microspheres.

## EPOXY ADHESIVE HAVING IMPROVED IMPACT RESISTANCE

5

## FIELD OF THE INVENTION

10 This invention relates to compositions useful as adhesives and more particularly to the preparation of epoxy-based adhesives with improved impact resistance capable of being employed with or without expansion agents.

## DISCUSSION OF THE RELATED ART

15 Numerous compositions and processes are described in the art for making and using a wide variety of epoxy-based compositions and other resins and additives in an effort to improve the expansion, impact resistance and other key properties of adhesives useful in adhering, filling and making composite structures. For example, patents which describe components for the formulation of adhesive compositions and the use of such

20 compositions to adhere various substrates to each other and to provide structural reinforcement include U.S. Pat. Nos. 5,334,654, 6,270,600, 6,332,731, 5,755,486, and 6,015,865. United States Pat. No. 5,278,257 describes a composition containing a) a copolymer based on at least one 1,3-diene and at least one polar, ethylenically unsaturated comonomer and b) a phenol-terminated polyurethane, polyurea, or

25 polyurea-urethane. Compositions containing components a) and b) as well as an epoxide resin are also described. United States Pat. No. 5,198,524 describes moisture-curing acrylate/epoxy hybrid adhesives containing a mixture of acrylate and epoxy with a tri- or tetrafunctional ketimine as a curing agent. The epoxy may be reacted with a chain extender having amine functionality, with the intermediate thereby

30 obtained being further reacted with an acrylated urethane. Nevertheless, significant problems remain with respect to the preparation of high impact epoxy based adhesives, especially when such adhesives are employed in an expanded state. Further, problems have existed in preparing high impact, expandable adhesives which can be flowed to the application site by pumping, for example, at ambient or moderately

35 elevated temperatures.

## SUMMARY OF THE INVENTION

We have discovered that unexpectedly improved adhesive formulations can be prepared by reacting a polyepoxide resin having at least about two 1,2-epoxy groups per molecule with an amino-terminated polyether and/or a carboxyl-containing 1,3-diene/polar ethylenically unsaturated comonomer resin (such as a carboxyl-terminated butadiene-nitrile rubber) to produce an epoxy-based prepolymer which is then admixed with an acrylate terminated urethane resin as defined herein (preferably, the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate), a latent curing agent capable of being activated by heat, and, optionally, fillers, coloring agents, expanding (blowing) agents, or other adjuvants of the type known in the art. When applied to a substrate or carrier and cured by heating, the adhesive results in a product having improved impact toughness and/or impact resistance useful in a wide variety of applications.

15

In a preferred embodiment, a curable adhesive is formulated which comprises:

A) an epoxy-based prepolymer obtained by reacting

(a) at least one epoxy resin prepared from bisphenol A or bisphenol F and epichlorohydrin having an epoxide equivalent weight of from about 150 to about 700; and

20

(b) at least one co-reactant selected from the group consisting of amino-terminated polyalkylene glycols (preferably, polyethylene and polypropylene glycols terminated with amine groups), carboxyl-terminated butadiene-nitrile resins, and mixtures thereof;

25

B) at least one acrylate-terminated urethane resin derived from a polyol having a number average molecular weight of at least about 400, a polyfunctional isocyanate, and an isocyanate-reactive acrylate and/or methacrylate; and

C) at least one heat-activated latent curing agent.

30

## DETAILED DESCRIPTION OF THE INVENTION

In a further preferred embodiment, the epoxy-based prepolymers useful in producing adhesive compositions of this invention are prepared in accordance with U.S. Patent

No. 6,015,865, which is hereby incorporated by reference in its entirety. In this preferred embodiment the epoxy-based prepolymer component is obtained by reacting

- a) an epoxy resin which is solid at room temperature;
- b) an epoxy resin which is liquid at room temperature; and
- 5 c) an amino-terminated polyether component selected from the group consisting of linear amino-terminated polyethylene glycols (ATPEGs), and linear and trifunctional amino-terminated polypropylene glycols (ATPPGs), the epoxy resins a) and b) being used in such a quantity that an excess of epoxide groups over the amino groups present in c) is ensured.

10

At this point mention is made that the components a), b) and c) can, in each case, also be mixtures of two or more compounds of the given type.

This epoxy-based prepolymer can be modified by adding other modified epoxy resins  
15 such as:

- i) adducts of dimeric fatty acids having varying molecular weights with epoxy resins of the diglycidyl ether type of bisphenol A or F (DGEBA or DGEBF) (e.g. Epikote® or EPON® 872),
- ii) adducts of carboxyl-terminated butadiene-nitrile rubber (CTBN) (Hycar®  
20 1300X8, 1300X13; Struktol®) with DGEBA or DGEBF

so that, even at high temperatures (up to +90° C) and under ageing conditions (including exposure to moisture), they exhibit permanent strength. Preferably 4 to 40, particularly 5 to 25, e.g. 20%, of the epoxide equivalents (EEW) of the total epoxy resin component may be replaced by such adducts.

25

When reacting the epoxy resins with the amino-terminated polyether, an excess of epoxy groups over the amino groups is preferably employed so that the latter react completely with epoxide groups. Typically, there is a 1.5 to 10-fold excess, for example, a 3.5-fold excess of EEW over the active hydrogen equivalents (AHEW) of the amines.

30 The rate of reaction may be accelerated by any suitable catalyst such as, for example, phosphines, amines, phosphonium salts, ammonium salts, or the like.

Carboxyl-containing resins which are copolymers of 1,3-dienes and polar ethylenically unsaturated monomers may also be used to prepare the epoxy-based prepolymer,  
35 either alone or in combination with one or more amino-terminated polyethers. The 1,3-

- diene is most preferably butadiene. The polar ethylenically unsaturated monomer is preferably acrylonitrile, although other suitable comonomers include methacrylonitrile, acrylic acid, methacrylic acid, esters and amides of acrylic and methacrylic acid, vinyl esters, and the like. Additional comonomers such as non-polar ethylenically
- 5 unsaturated monomers may also be present. The carboxyl functionality may be introduced onto these resins by any suitable means. The composition of the carboxyl-containing resin should be selected such that the glass transition temperature of the resin is less than about -30 degrees C. Especially preferred for use are the carboxyl-terminated butadiene-nitrile rubbers, such as those for example sold under the HYCAR
- 10 trademark by B.F. Goodrich (in particular, HYCAR CTBN 1300 X 8, HYCAR CTBN 1300 X 13, and HYCAR CTBN 1300 X 15) . The carboxyl-terminated butadiene-nitrile rubber preferably has a number average molecular weight of from about 2000 to about 5000 and an acrylonitrile content of from about 10 to about 30 weight percent. The carboxyl-containing resins may be reacted with one or more epoxy resins to form the
- 15 epoxy-based prepolymer by any suitable method, such as heating these components under conditions effective to cause reaction while avoiding complete curing of the epoxy resins. A catalyst such as an amine, phosphine, ammonium salt, phosphonium salt, or the like may be utilized.
- 20 The epoxy-based prepolymer is then admixed with an acrylate terminated urethane resin as described herein and a latent curing agent (as well as with other desired additives) to prepare an improved curable adhesive for use in expanded or non-expanded applications where high impact resistance is needed.
- 25 The adhesive made according to this invention exhibits high T-peel and impact peel strengths in the temperature range of -40° C to +90° C. In the cured state, these adhesives display the degree of flexibility which is necessary especially in the manufacture of automobiles and trucks. The flexibility of the resin matrix may be adjusted by using amino-terminated polyether of varying functionality (bi- or
- 30 trifunctional) and variable chain-length, and by varying the ratio of amino-terminated polyether to epoxy resin. The impact toughness and flowability at ambient temperatures may be adjusted by varying the ratio of epoxy-based prepolymer to the acrylate functional urethane resin or resins.

The weight ratio of epoxy-based prepolymer to acrylate terminated urethane resin is preferably between about 50:1 to about 1:1 - and most preferably between about 20:1 to about 4:1.

- 5 Preferably, the molar amount of acrylate groups in the adhesive is less than 10 % (more preferably, less than 5 %) of the total molar amount of acrylate and epoxy groups in the adhesive. In contrast, the compositions described in U.S. Pat. No. 5,198,524 require acrylate levels of at least 10 mole %, preferably at least 30 mole %.
- 10 Surprisingly, the curable adhesives made by combining the epoxy-based prepolymer with the acrylate terminated urethane resin and a latent curing agent may be formulated to be pumpable at ambient temperatures or slightly higher, e.g., between about 10 to about 50 degrees C, preferably between about 20 and about 40 degrees C and have improved peel strengths both in the expanded and unexpanded cured state over the
- 15 prior art.

In general, a large number of polyepoxides having at least two 1,2-epoxy groups per molecule are suitable as epoxy resins for making the epoxy-based prepolymer employed in this invention. The polyepoxides may be saturated, unsaturated, cyclic or

20 acyclic, aliphatic, alicyclic, aromatic or heterocyclic polyepoxide compounds. Examples of suitable polyepoxides include the polyglycidyl ethers, which are prepared by reaction of epichlorohydrin or epibromohydrin with a polyphenol in the presence of alkali. Suitable polyphenols therefor are, for example, resorcinol, pyrocatechol, hydroquinone, bisphenol A (bis(4-hydroxyphenyl)-2,2-propane), bisphenol F (bis(4-hydroxyphenyl)methane), bis(4-

25 hydroxyphenyl)-1,1-isobutane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, and 1,5-hydroxynaphthalene. Other suitable polyphenols as the basis for the polyglycidyl ethers are the known condensation products of phenol and formaldehyde or acetaldehyde of the novolak resin-type.

30 Other polyepoxides that are in principle suitable are the polyglycidyl ethers of polyalcohols or diamines. Such polyglycidyl ethers are derived from polyalcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol or trimethylolpropane.

35 Other polyepoxides are polyglycidyl esters of polycarboxylic acids, for example, reaction

products of glycidol or epichlorohydrin with aliphatic or aromatic polycarboxylic acids, such as oxalic acid, succinic acid, glutaric acid, terephthalic acid or a dimeric fatty acid.

5 Other epoxides are derived from the epoxidation products of olefinically-unsaturated cycloaliphatic compounds or from natural oils and fats.

Particular preference is given to the epoxy resins derived by reaction of bisphenol A or bisphenol F and epichlorohydrin, the liquid epoxy resins preferably being based on bisphenol A and having a sufficiently low molecular weight. The epoxy resins that are  
10 liquid at room temperature generally have epoxy equivalent weights of from 150 to about 480; particular preference is given to an epoxy equivalent weight range of from 182 to 350. Liquid epoxy resins of this type may be utilized in unreacted form as additional components of the curable adhesives of the present invention.

15 The epoxy resins that are solid at room temperature are likewise obtainable from polyphenols and epichlorohydrin; particular preference is given to those based on bisphenol A or bisphenol F having a melting point of from 45 to 130 degrees C, preferably from 50 to 80 degrees C. They differ from the liquid epoxy resins substantially by the higher molecular weight thereof, as a result of which they become solid at room  
20 temperature. According to the present invention, the solid epoxy resins have an epoxy equivalent weight of  $\geq 400$ ; particular preference is given to an epoxy equivalent weight of from 450 to about 900.

The curable adhesives of the present invention may additionally comprise one or more  
25 further flexibility-conferring components such as those conventionally used for such purpose in the epoxy resin art. Particular preference is given, however, to the adducts (reaction products) of polymeric fatty acids, especially of dimeric fatty acids, with epoxides such as epichlorohydrin, glycidol or, especially, the diglycidyl ethers of polyphenols such as bisphenol A (DGBA). Also preferred for use (especially where the epoxy-based  
30 prepolymer has been obtained by reacting an epoxy resin with an amino-terminated polyether) are the adducts (reaction products) of carboxy-terminated butadiene-nitrile rubbers with epoxy resins (especially liquid diglycidyl ethers of polyphenols such as bisphenol A). These further flexibility-conferring components may be admixed with the epoxy-based prepolymer following preparation of such prepolymer or, in a preferred  
35 embodiment, be present during reaction of the materials used to prepare the epoxy-based

prepolymer.

Since the curable adhesives of the present invention are preferably one-part or single-component compositions and are to be cured at elevated temperature, they also contain  
5 one or more hardeners capable of accomplishing cross-linking or curing of certain of the adhesive components when the adhesive is heated to a temperature well in excess of room temperature. That is, the hardener is activated by heating, in contrast to the ketimine hardeners of U.S. Pat. No. 5,198,524, which are activated by exposure to moisture. The hardener may function in a catalytic manner or, in preferred embodiments  
10 of the invention, participate directly in the curing process by reaction with one or more of the adhesive components.

There may be used as thermally-activatable or latent hardeners for the adhesive compositions of the present invention, for example, guanidines, substituted guanidines,  
15 substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines and/or mixtures thereof. The hardeners may be involved stoichiometrically in the hardening reaction; they may, however, also be catalytically active. Examples of substituted guanidines are methylguanidine, dimethylguanidine, trimethylguanidine, tetramethylguanidine, methylisobiguanidine, dimethylisobiguanidine,  
20 tetramethylisobiguanidine, hexamethylisobiguanidine, heptamethylisobiguanidine and, more especially, cyanoguanidine (dicyandiamide). Representatives of suitable guanamine derivatives which may be mentioned are alkylated benzoguanamine resins, benzoguanamine resins or methoxymethylethoxymethylbenzoguanamine. For single-component, thermosetting adhesives, the selection criterion is, of course, the low solubility  
25 of those substances at room temperature in the resin system, so that solid, finely ground hardeners are preferred; dicyandiamide is especially suitable. Good storage stability of the composition is thereby ensured.

In addition to or instead of the above-mentioned hardeners, catalytically-active substituted  
30 ureas may be used. They are especially *p*-chlorophenyl-N,N-dimethylurea (monuron), 3-phenyl-1,1-dimethylurea (fenuron) or 3,4-dichlorophenyl-N,N-dimethylurea (diuron). In principle, catalytically active tertiary acryl- or alkyl-amines, such as benzyldimethylamine, tris(dimethylamino)phenol, piperidine or piperidine derivatives, may also be used, but they are in many cases too highly soluble in the adhesive system, so that usable storage  
35 stability of the single-component system is not achieved. Various imidazole derivatives,



preferably solid imidazole derivatives, may also be used as catalytically-active accelerators. Examples which may be mentioned are 2-ethyl-2-methylimidazole, N-butylimidazole, benzimidazole and N-C<sub>1</sub> to C<sub>12</sub>-alkylimidazoles or N-arylimidazoles. Particular preference is given to the use of a combination of hardener and accelerator in the form of so-called accelerated dicyandiamides in finely ground form. The separate addition of catalytically-active accelerators to the epoxy hardening system is thus not necessary.

The adhesives according to the present invention may also contain known fillers such as the various ground or precipitated chalks, carbon black, calcium magnesium carbonates, barite and, especially, silicate-like fillers of the aluminum magnesium calcium silicate type, for example wollastonite and chlorite.

When it is desirable to make lightweight (low density) structures, the adhesives preferably contain in addition to the above-mentioned fillers so-called lightweight fillers, which are selected from hollow glass spheres, flue ash, mica, hollow plastic spheres based on phenol resins, epoxy resins or polyesters, hollow ceramic spheres, or organic lightweight fillers of natural origin, such as ground nutshells, for example the shells of cashew nuts, coconuts or groundnut shells, as well as cork powder or coke powder. Particular preference is given to such lightweight fillers based on hollow glass or ceramic microspheres.

In another embodiment, the curable adhesive composition additionally contains fibers based on aramide fibers, carbon fibers, glass fibers, polyamide fibers, polyethylene fibers or polyester fibers, those fibers preferably being pulp fibers or staple fibers having a fiber length of from 0.5 to 6 mm and a diameter of from 5 to 20 microns. Particular preference is given to polyamide fibers of the aramide fiber type, or to polyester fibers.

In one particularly preferred embodiment of the invention, the curable adhesive contains one or more expanding agents (sometimes referred to in the art as blowing agents). The expandable properties of the resulting adhesive are particularly useful in applications where the complete filling of a gap or cavity in a part or member is critical in order to maintain maximum structural integrity of the part or member. The foamed cured adhesive has improved fracture toughness, thereby imparting impact resistance to the assembly. If the curable adhesive is to be utilized as a one-part or single-component composition, the

expanding agent is preferably a latent expanding agent which causes expansion or foaming of the adhesive only when heated to a temperature significantly above room temperature (typically, a temperature which is in the range at which curing of the adhesive is also initiated). Although any suitable expanding agent may be employed, such as a

5 chemical expanding agent, e.g., azo compounds, hydrazides and the like, particular preference is given to expandable microspheres. Expandable microspheres generally comprise small diameter polymeric shells or bubbles which encapsulate one or more volatile substances such as light hydrocarbons or halocarbons. The outer shells are usually thermoplastic in character to permit softening and expansion of the microspheres

10 when heated due to volatilization of the substances trapped within the shells. The polymers used in the shells may be linear, branched, or cross-linked and may be comprised of, for example, acrylic resins, styrenic resins, polyvinylidene chloride, nitrile polymers, and the like. Typically, the average particle size of the expandable microspheres is in the range of from about 5 to about 100 microns. Suitable expandable

15 microspheres are commercially available under the trademark names DUALITE and EXPANCEL from Pierce & Stevens and Casco Nobel, respectively. In one embodiment of the invention, the type and amount of expanding agent(s) are selected such that the curable adhesive expands in volume between about 90% and about 130% when heated and cured.

20 The adhesive compositions according to the present invention may also contain other common adjuvants and additives, such as plasticizers, reactive and/or non-reactive diluents, flow auxiliaries, wetting agents, tackifiers, flame retardants, thixotropic and/or rheology control agents, ageing and/or corrosion inhibitors, stabilizers and/or coloring

25 pigments. Depending on the requirements made of the adhesive application with respect to its processing properties, its flexibility, the required rigidifying action and the adhesive bond to the substrates, the relative proportions of the individual components may vary within comparatively wide limits. Typical ranges for the main components of the curable adhesive of the present invention are as follows:

30	a)	epoxy-based prepolymer	from 10 to 70 wt. %
	b)	acrylate-terminated urethane	from 1 to 15 wt. %
	c)	liquid epoxy resins	from 10 to 50 wt. %
	d)	hardener/accelerator	from 0.5 to 10 wt. %
	e)	expanding agent	from 0 to 5 wt. %
35	f)	lightweight filler	from 0 to 50 wt. %

- |    |          |                    |
|----|----------|--------------------|
| g) | fillers  | from 3 to 30 wt. % |
| h) | fibers   | from 0 to 5 wt. %  |
| i) | pigments | from 0 to 1 wt. %  |

5 In the cured state, one or more of the following improvements may be achieved as compared with the prior art:

- higher impact resistance or toughness in expanded and unexpanded applications
- improved flow characteristics at ambient temperatures which permit pumping to  
10 the worksite at temperatures well below cure temperatures
- higher resistance to pressure
- lower brittleness
- improved resistance to cold and heat
- reduced temperature dependence of the resistance to pressure from  $-30^{\circ}\text{C}$  to  
15  $+90^{\circ}\text{C}$
- constant force level over the deformation path
- reduction in density (specific weight)
- low water absorption

20 In the preparation of the epoxy-based prepolymer, the following compounds may, for example, be used as amino-terminated polyethylene glycols (ATPEG) or polypropylene glycols (ATPPG):

1. linear amino-terminated polyethylene glycols (ATPEG) having the formula:

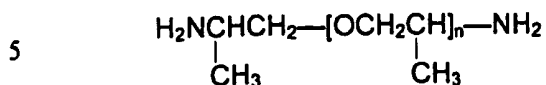
25



in which n preferably is 17 to 27.

30

2. linear amino-terminated polypropylene glycols (ATPPG) having the formula:



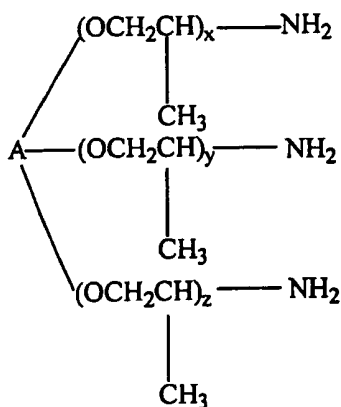
in which n preferably is 5 to 100. They are obtainable from Huntsman Chemical under the trade name Jeffamine® (D-series).

10

Jeffamine® Type	n	approx. molecular weight
D-400	5-6	400
D-2000	33	2000
D-4000	68	4000

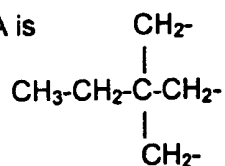
15

3. trifunctional compounds having the formula:



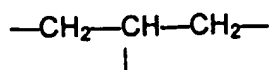
20

in which A is



25

or a



5

group and x, y and z independently of each other are 1 to 40 and x+y+z is preferably >6. They are obtainable from Huntsman Chemical under the trade name Jeffamine® (T-series).

10	Jeffamine® Type	A (initiator)	approx. molecular weight
	T-403	trimethylol propane	440
15	T-3000	glycerin	3000
	T-5000	glycerin	5000

20 Amino-terminated polyalkylene glycols containing both oxyethylene and oxypropylene repeating units may also be utilized as the amino-terminated polyether. Preferably, the amino-terminated polyether contains at least two amine groups per molecule. Preferably, the amine groups are primary amine groups. The amino-terminated polyether is preferably aliphatic. In addition to the aforescribed amino-terminated polyethylene glycols, polypropylene glycols, and mixed polyethylene-propylene glycols, 25 other aliphatic polyethers containing terminal amine groups such as amino-terminated polytetramethylene glycols or amino-terminated polybutylene glycols or mixed polypropylene-butylene glycols may be used.

30 As already mentioned, the properties of the curable adhesive can be controlled by varying the ratios of the resin components especially the ratio of the epoxy-based prepolymer and the acylate terminated urethane resin according to the present invention. Referring to the epoxy-based prepolymer in a preferred embodiment, 0.5 to 1 equivalent (30 to 50 wt-%) of epoxy resin a) which is solid at room temperature and 0.5 to 1 equivalent (10 to 25 wt-%) of epoxy resin b) which is liquid at room temperature are 35 reacted with 0.125 to 0.5 equivalent (35 to 50 wt-%) of the amino-terminated polyethylene or polypropylene glycols, it being possible for 0.5 to 10 wt-% to be a trifunctional ATPPG. The heat-resistance of the curable adhesive can be further

improved by adding dimeric acid and/or butadiene-nitrile rubber/DGEBA or DGEBF adducts. More specifically, the epoxy-based prepolymer can be modified by adding other modified epoxy resins such as :

- 5           i)    adducts of dimeric fatty acids having varying molecular weights with epoxy resins of the diglycidyl ether type of bisphenol A or F (DGEBA or DGEBF) (e.g. Epikote® or EPON® 872); and/or
- ii)   adducts of carboxyl-terminated butadiene-nitrile rubber (CTBN) (Hycar® 1300X8, 1300X13; Struktol®) with DGEBA or DGEBF.

10   The adducts of type ii) may be used by themselves as the epoxy-based prepolymer component of the present invention.

When reacting the epoxy resins with the ATPEG/ATPPG, an excess of epoxy groups over the amino groups is used so that the latter react completely with epoxide groups. Typically, there is a 1.5 to 10-fold excess, for example a 3.5-fold excess of EEW over  
15   the active hydrogen equivalents (AHEW) of the amino-terminated polyether. In preparing the curable adhesive according to the present invention, the epoxy-based prepolymer component preferably is initially prepared in a first stage. To this end, preferably, the epoxy resins (such as, for example, solid epoxy resin a) and the liquid epoxy resin b)) are reacted with the amino-terminated polyether c) in the desired ratio.  
20   The reaction preferably is carried out at high temperature, preferably at 90 to 130° C., for example at approximately 120°C., for a duration of e.g. three hours.

The resultant epoxy-based prepolymer may be formulated to be solid or viscous at room temperature. It can be directly further processed by admixture with the acrylate  
25   terminated urethane resin and latent curing agent to obtain the curable adhesive according to this invention. However, it is also possible to prepare the epoxy-based prepolymer in advance and to store it until further processing. For further processing, first of all it may be necessary to heat the epoxy-based prepolymer in order to lower its viscosity to such a degree that it can be mixed with the other constituents of the curable  
30   adhesive. The prepolymer is preferably heated to a temperature above 50°C., for example 60 to 110°C., particularly 70 to 95°C. Then the other modified resins including the acrylate terminated urethane resin are added and homogeneously mixed. It must be ensured that heating is not carried out to a temperature at which the added latent curing agent would be activated. For heating the epoxy-based prepolymer and mixing with the  
35   other constituents of the curable adhesive, a heated kneader or planetary mixer is

suitably used. It is preferred to incorporate the latent curing agent in the mixture last after the other constituents. It is further preferred to cool the mixture, prior to adding the latent curing agent, to a temperature at the lower limit of the temperature range which is suitable for processing.

5

In accordance with this invention, the epoxy-based prepolymer prepared as described above is mixed with an acrylate terminated urethane resin and more preferably with one or more acrylate terminated urethanes such as those described in U.S. Pat. Nos. 3,297,745; 4,360,653; 4,390,662; 4,719,268; 4,486,582; 4,618,658; 5,334,654; and  
10 5,700,891 which are hereby incorporated by reference in their entirety. Acrylate-terminated urethane resins comprise the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate and/or methacrylate. Isocyanate terminated prepolymers are prepared by reacting a polyfunctional isocyanate, typically an aromatic diisocyanate, with a polyol, preferably a long chain  
15 hydroxyl-terminated polyether or polyester polyol, such as the ethylene and propylene oxide adducts of C<sub>2</sub> to C<sub>4</sub> polyalcohols, polytetramethylene glycol (polyTHF), and polycaprolactone. For enhanced flexibilization of the cured adhesive, the molecular number average weight of the polyol should range from about 400 to 4000, preferably 700 to 2000. Acrylate terminated urethane resins utilizing a polyol having a number  
20 average molecular weight of less than 1000 generally are extremely viscous. Higher molecular weight polyols tend to cause premature phase separation in the formulated adhesive leading to poor physical properties. The preferred isocyanate-terminated urethane prepolymer is prepared by any known means, for example, a 2000 mw polypropylene glycol may be reacted with an 80/20 2,4/2,6-toluenediisocyanate mixture.  
25 Any other polyisocyanate such as methylenediphenyldiisocyanate (MDI), isophoronediiisocyanate, (IPDI) or paraphenylenediisocyanate (PPDI) is also suitable.

The isocyanate-reactive acrylates and methacrylates ("(meth)acrylates") typically used to prepare the acrylate terminated urethane prepolymers are hydroxy alkylacrylates and  
30 methacrylates and these include: hydroxyacrylates such as hydroxyethyl acrylate or methacrylate, hydroxypropyl acrylate or methacrylate, hydroxypentyl acrylate or methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl hexyl methacrylate, hydroxybutyl methacrylate and the like. Typically the ester portion of the acrylate or methacrylate is from a C<sub>2</sub>-C<sub>8</sub> alcohol. Mixtures of different (meth)acrylates may be used.

35

Additional materials which can be used to prepare substances which we choose to describe as included within the definition of acrylate-terminated urethane resins include the following:

- 5           1) prepolymers having number average molecular weights of 250-10,000, preferably 700-4000, and having glass transition temperatures below about 10 degrees C, preferably below about minus 10 degrees C. The average functionality of these prepolymers is at least 2, preferably 2 to 6 and particularly preferably 2 to 3. The terminal functional groups of the prepolymer are isocyanate-reactive and may be amino or hydroxyl or carboxyl or mercapto, preferably, hydroxyl.

10           Particularly preferred prepolymers include linear and branched polypropylene glycols having number average molecular weights about 700 to about 4000; linear and branched polytetrahydrofurans having number average molecular weights between about 700 and about 4000; linear and branched poly(1,2-buyleneoxide) having number average molecular weights between about 700 and about 4000; and hydroxyl-terminated polyesters having number average molecular weights between about 700 and about 4000.

- 15           2) polyisocyanates, preferably diisocyanates or triisocyanates such as isophoronediisocyanate, methylenediphenyldiisocyanate, toluenediisocyanate, hexamethylenediisocyanate, tetramethylxylylenediisocyanate, and the like.
- 20           3) isocyanate-reactive acrylates or methacrylates, preferably hydroxyacrylates or -methacrylates such as hydroxyethylacrylate, hydroxypropylacrylate, hydroxyethylmethacrylate, hydroxypropylmethacrylate, and the like.

25           Chain lengtheners such as diols and triols like 1,4 butanediol, 1,1,1-trimethylolpropane, glycerol, 1,2,6-hexanetriol, pentaerythritol and the like optionally may be employed in combination with the polyol(s), preferably, from 0.01 to about 5% by weight. When triol chain lengtheners, as described above, are added during this reaction and a suitable amount of polyisocyanate is used, branched NCO-tipped prepolymers are produced.

30           Diol chain lengtheners can be used to control the molecular weight of the resulting prepolymer. This NCO-functional polymer is then reacted with the NCO-reactive acrylate or methacrylate to yield materials which are described for the purposes of this invention as acrylate-terminated urethane resins.

35



In another embodiment within the scope of this invention, the acrylate-terminated urethane resins as described herein may also be employed as an adduct onto an epoxy resin (e.g., the acrylate-terminated urethane resin is reacted with an epoxy resin before being combined with other components of the curable adhesive).

5

It should be further understood that in yet another embodiment within the scope of the present invention, an acrylate terminated urethane resin is employed to produce a curable adhesive composition without employing the amine-terminated polyether materials described above by admixing an epoxide resin having at least two 1,2-epoxide groups per molecule as described herein, a copolymer based on at least one 1,3-diene and at least one polar, ethylenically unsaturated comonomer, such as acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, or esters of acrylic or methacrylic acid with C<sub>1</sub>-C<sub>6</sub> alcohols and a heat-activated latent curing agent as described herein.

15

The reactive adhesive according to the invention is suitable for gluing or adhering parts made of different materials. It is preferably used for the gluing of metal parts and particularly for the gluing of steel sheets. These can also be electro-galvanized, hot-dip galvanized or zinc/nickel-coated steel sheets, for example.

20

The adhesive may be deposited in the form of a melt on one side, i.e., onto one of the two parts which are to be glued together. In one embodiment of the invention, the adhesive is formulated so as to function as a hot melt; that is, an adhesive which is solid at room temperature, but capable of being converted to a pumpable or flowable material when heated to a temperature above room temperature. In another embodiment, the curable adhesive composition of this invention is formulated to be capable of being flowed or pumped to the work site at ambient temperatures or slightly above since, in most applications, it is preferable to ensure that the adhesive is heated only up to a temperature at which the latent curing agent is not yet activated. In yet another embodiment, the curable adhesive is formulated (by inclusion of a finely divided thermoplastic or by use of multiple curatives having different activation temperatures, for example) such that the curing process proceeds in two or more stages (partial curing at a first temperature, complete curing at a second, higher temperature). The two parts are joined together, preferably immediately after deposition of the adhesive mass, thereby provisionally bonding the two parts to each other.

35

The resultant bond preferably already has sufficient strength so that the still uncured adhesive is not readily washed out, as might otherwise occur, for example, if the metal sheets which are provisionally bonded to each other are treated for de-greasing purposes in a wash bath and then in a phosphating bath.

The adhesive is preferably finally cured in an oven at a temperature which lies clearly above the temperature at which the curable adhesive was applied to the parts to be bonded and at or above the temperature at which the hardener and/or accelerator and/or latent expanding agent (if present) are activated (i.e., in the case of the hardener, the minimum temperature at which the hardener becomes reactive towards the other components of the adhesive; in the case of the expanding agent, the minimum temperature at which the expanding agent causes foaming or expansion of the adhesive). Curing preferably takes place at a temperature above 150°C, for example at 160 to 170°C, for about 30 minutes.

Once cured, the adhesive compositions according to the present invention may be used as casting resins in the electrical or electronics industry or as die attach adhesives in electronics for bonding components to printed circuit boards. Further possible applications for the curable adhesives are as matrix materials for composites, such as fiber-reinforced composites. One particularly preferred application for the adhesives according to the present invention is the formation of structural bonds in vehicle construction.

In the embodiment of the invention wherein the curable adhesive contains one or more expanding agents, the adhesive may be utilized to form structural foams which serve to stiffen and reinforce cavities, gaps, structural members and the like. The curable adhesive may be supported or contained within a carrier or receptacle or the like so as to position or orient the adhesive such that it expands in one or more particular directions when heated to induce curing and foaming. The curable adhesive thus is particularly useful in filling irregularly shaped spaces, as the adhesive will expand so as to come into contact with a greater portion of the substrate surfaces in the vicinity of the adhesive than would occur if no expanding agent was present. The foamed, cured adhesive stiffens and/or increases the energy absorption capacity of vehicle cavities and structural members.

**EXAMPLE 1 – PREPARATION OF EPOXY-BASED PREPOLYMER SF 65**

- The reaction products of linear and trifunctional ATPPG with DGEBA can be prepared separately or in the mixture. Epoxy-based prepolymers A to J were prepared from the following constituents, the formulation size being 1 kg in each case:

**Preparation of Epoxy-Based Prepolymers (in equivalents)**

	EEW	AHEW	A	B	C	D	E	F	G	H	J
liquid DGEBA	187		0.765	0.765	0.765	0.765	0.69	0.765	-	1.785	-
semisolid DGEBA	255		-	-	-	-	-	-	1.122	-	1.122
solid DGEBA	475		0.765	0.765	0.765	0.765	0.692	-	-	-	-
solid DGEBA	537		-	-	-	-	-	0.266	-	-	-
CTBN adduct	325		0.17	0.17	0.17	0.17	-	-	0.147	-	-
CTBN adduct	190*		-	-	-	-	-	0.125	-	-	0.125
Dimeric fatty acid/epoxy resin adduct	650		-	-	-	-	0.34	-	-	-	-
Linear ATPPG		1000	0.44	0.43	0.44	0.43	0.43	-	-	-	-
Linear ATPPG		500	-	-	-	-	-	0.334	0.286	0.238	0.334
trifunct. ATPPG		500	0.08	0.023	-	-	0.013	-	-	0.048	-
trifunct. ATPPG		75	-	-	0.011	0.023	-	-	-	-	-
Viscosity at 80°C [Pa•s]			36	37	28	33	34	17	6.3	0.59	7.8

\*5% CTBN, 95% DGEBA

- The epoxy resins were melted at approximately 80°C and introduced first into the kneader by means of a delivery screw, then the additional components were added and homogeneously mixed at 80°C.

Abbreviations used herein are defined as follows:

- CTBN = carboxyl-terminated butadiene-nitrile rubber  
 ATPPG = amino-terminated polypropylene glycol  
 5 DGEBA = diglycidyl ether of bisphenol A  
 EEW = epoxide equivalent weight  
 AHEW = active hydrogen equivalent weight  
 TSS = tensile shearing strength  
 TPS = t-peel strength  
 10 SF-65 = the epoxy-based prepolymer product resulting from the above procedure

#### EXAMPLE 2 – PREPARATION OF THE ACRYLATE TERMINATED URETHANE RESIN

- 15 The NCO-reactive components (polyols) are mixed for 45 min at 90-100°C and 0.1-2 mbar to remove water. The polyisocyanate is then added in one portion under nitrogen at 50°C. The reaction mixture is mixed under nitrogen at 70-80°C to a constant NCO-value. Then the NCO-reactive acrylate is added together with a polymerization inhibitor. Dibutyltin dilaurate (0.01%) is added after 1 hour at 80°C and the mixing is continued  
 20 for additional 2 h, then the epoxy resin is added.

Acrylate Terminated Urethane Resin A:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
CAPA 305	275	10.7	Polycaprolactone Polyol	Solvay Interlox
CAPA 220	672	26.2	Polycaprolactone Polyol	Solvay Interlox
MDI	538	21.0	Methylenediphenyldiisocyanate	
HPMA	310	12.1	Hydroxypropyl methacrylate	
EPON 828	769	30.0	DGEBA	Resolution Performance Products

**Acrylate Terminated Urethane Resin B:**

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PTHF 650	392	39.0	Polytetrahydrofuran	
MDI	225	22.4	Methylenediphenyldiisocyanate	
HPMA	86	8.6	Hydroxypropyl methacrylate	
EPON 828	301	30.0	DGEBA	Resolution Performance Products

5 **Acrylate Terminated Urethane Resin C:**

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PTHF 650	398	40.0	Polytetrahydrofuran	
MDI	225	22.6	Methylenediphenyldiisocyanate	
HEA	73	7.3	Hydroxyethyl acrylate	
EPON 828	298	30.0	DGEBA	Resolution Performance Products

**Acrylate Terminated Urethane Resin D:**

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
CAPA 305	110	11.0	Polycaprolactone Polyol	Solvay Interlox
CAPA 220	267	26.7	Polycaprolactone Polyol	Solvay Interlox
MDI	217	21.7	Methylenediphenyldiisocyanate	
HEA	106	10.6	Hydroxyethyl acrylate	
EPON 828	300	30.0	DGEBA	Resolution Performance Products

## Acrylate Terminated Urethane Resin E:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
DYNACOLL 7250	612	61.2	Polyester Polyol	Degussa
MDI	59	5.9	Methylenediphenyldiisocyanate	
HEA	29	2.9	Hydroxyethyl acrylate	
EPON 818	300	30.0	DGEBA	Resolution Performance Products

## Acrylate Terminated Urethane Resin F:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
DYNACOLL 7360	589	58.9	Polyester Polyol	Degussa
MDI	75	7.5	Methylenediphenyldiisocyanate	
HEA	36	3.6	Hydroxyethyl acrylate	
EPON 828	300	30.0	DGEBA	Resolution Performance Products

5

## Acrylate Terminated Urethane Resin G:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 900	551	45.4	Polypropylene glycol	BASF
MDI	225	18.5	Methylenediphenyldiisocyanate	
HEA	73	6.0	Hydroxyethyl acrylate	
EPON 828	364	30.0	DGEBA	Resolution Performance Products

10

## Acrylate Terminated Urethane Resin H:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 2000	1225	56.3	Polypropylene glycol	BASF
MDI	225	10.3	Methylenediphenyldiisocyanate	
HEA	73	3.4	Hydroxyethyl acrylate	
EPON 828	653	30.0	DGEBA	Resolution Performance Products

## Acrylate Terminated Urethane Resin J:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 900	551	46.8	Polypropylene glycol	BASF
IPDI	200	17.0	Isophorone diisocyanate	
HEA	73	6.2	Hydroxyethyl acrylate	
EPON 828	353	30.0	DGEBA	Resolution Performance Products

5

## Acrylate Terminated Urethane Resin K:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 2000	1225	57.2	Polypropylene glycol	BASF
IPDI	200	9.3	Isophorone diisocyanate	
HEA	73	3.4	Hydroxyethyl acrylate	
EPON 828	642	30.0	DGEBA	Resolution Performance Products

## 10 Acrylate Terminated Urethane Resin L:

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 900	551	49.8	Polypropylene glycol	BASF
HDI	151	13.6	Hexamethylene diisocyanate	
HEA	73	6.6	Hydroxyethyl acrylate	
EPON 828	332	30.0	DGEBA	Resolution Performance Products

**Acrylate Terminated Urethane Resin M:**

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
PLURIOL P 2000	425	54.8	Polypropylene glycol	BASF
Trimethylol propane	2.2	0.28		
HDI	65	8.4	Hexamethylene diisocyanate	
HEA	51	6.6	hydroxyethyl acrylate	
EPON 828	233	30.0	DGEBA	Resolution Performance Products

**Acrylate Terminated Urethane Resin N:**

Component	Weight in grams	Weight percent	Chemical name of component	Tradename of Company
ANCAREZ 2364	1000	100.0	Acrylate-functional urethane resin	Air Products

5

**EXAMPLE 3 - PREPARATION OF THE CURABLE ADHESIVE**

Curable adhesives are prepared by admixing SF-65 with an acrylate-terminated urethane resin and other components listed in Table 1 below with mixing for 45 minutes at a temperature controlled between 27-38 degrees C (80-100 degrees F) and pressure of 0.3-3psi.

10



**TABLE 1**

(all amounts stated are in grams)

Component / Adhesive	1	2	3	4	5	6	7	8	9	10	11	12
SF-65 A (Example 1)	500									500	500	500
SF-65 B (Example 1)		500										
SF-65 C (Example 1)			500									
SF-65 D (Example 1)				500								
SF-65 E (Example 1)					500							
SF-65 F (Example 1)						500						
SF-65 G (Example 1)							500					
SF-65 H (Example 1)								500				
SF-65 J (Example 1)									500			
Polydis 3604												
EPON 828	100	100	100	100	100	100	100	100	100	100	100	100
EPON 834												
DER 351	100	100	100	100	100	100	100	100	100	100	100	100
DER 354												
Resin A (Example 2)										100		
Resin B (Example 2)											100	
Resin C (Example 2)												100
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)												
Resin H (Example 2)												
Resin J (Example 2)	100	100	100	100	100	100	100	100	100			
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)												
Resin N (Example 2)												
AMICURE CG 1400	50	50	50	50	50	50	50	50	50	50	50	50
DE 83R	20	20	20	20	20	20	20	20	20	20	20	20
BUSAN 11-M1	10	10	10	10	10	10	10	10	10	10	10	10
Calcium Oxide	10	10	10	10	10	10	10	10	10	10	10	10
MONARCH 280	5	5	5	5	5	5	5	5	5	5	5	5
ULTRA PFLEX	29	29	29	29	29	29	29	29	29	29	29	29
DYHARD UR 300	6	6	6	6	6	6	6	6	6	6	6	6
EXPANCEL 551	10	10	10	10	10	10	10	10	10	10	10	10
Cab-O-Sil TS 720	30	30	30	30	30	30	30	30	30	30	30	30
EPODIL 749	30	30	30	30	30	30	30	30	30	30	30	30

Component / Adhesive	13	14	15	16	17	18	19	20	21	22	23	24
SF-65 A (Example 1)	500	500	500	500	500	500	500	500	500	480		
SF-65 B (Example 1)												
SF-65 C (Example 1)											480	
SF-65 D (Example 1)												
SF-65 E (Example 1)												
SF-65 F (Example 1)												
SF-65 G (Example 1)												
SF-65 H (Example 1)												480
SF-65 J (Example 1)												
Polydis 3604										106	106	106
EPON 828	100	100	100	100	100	100	100	100	100	106	106	106
EPON 834												
DER 351	100	100	100	100	100	100	100	100	100			
DER 354												
Resin A (Example 2)										89		
Resin B (Example 2)												
Resin C (Example 2)												
Resin D (Example 2)	100											
Resin E (Example 2)		100										
Resin F (Example 2)			100									
Resin G (Example 2)				100								
Resin H (Example 2)					100						89	89
Resin J (Example 2)												
Resin K (Example 2)						100						
Resin L (Example 2)							100					
Resin M (Example 2)								100				
Resin N (Example 2)									100			
AMICURE CG 1400	50	50	50	50	50	50	50	50	50	65	65	65
DE 83R	20	20	20	20	20	20	20	20	20			
BUSAN 11-M1	10	10	10	10	10	10	10	10	10	37	37	37
Calcium Oxide	10	10	10	10	10	10	10	10	10			
MONARCH 280	5	5	5	5	5	5	5	5	5	7	7	7
ULTRA PFLEX	29	29	29	29	29	29	29	29	29	300	300	300
DYHARD UR 300	6	6	6	6	6	6	6	6	6	7	7	7
EXPANCEL 551	10	10	10	10	10	10	10	10	10	8.4	8.4	8.4
Cab-O-Sil TS 720	30	30	30	30	30	30	30	30	30	41	41	41
EPODIL 749	30	30	30	30	30	30	30	30	30	37	37	37

Component / Adhesive	25	26	27	28	29	30	31	32	33	34	35	36
SF-65 A (Example 1)											778	
SF-65 B (Example 1)						230						
SF-65 C (Example 1)	480		480									
SF-65 D (Example 1)												865
SF-65 E (Example 1)								500	500			
SF-65 F (Example 1)					190					628		
SF-65 G (Example 1)												
SF-65 H (Example 1)		480		480								
SF-65 J (Example 1)							271					
Polydis 3604	106	106	106	106	80	50		90	90			
EPON 828	106	106	106	106	150	200	388	600	600	600	250	
EPON 834					60			120	120	108	100	
DER 351					60							300
DER 354							33			100	200	
Resin A (Example 2)												
Resin B (Example 2)												
Resin C (Example 2)			89	89								
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)					130							
Resin H (Example 2)												
Resin J (Example 2)												
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)	89	89							200		130	280
Resin N (Example 2)						80	50	200		100		
AMICURE CG 1400	65	65	65	65	55	50	57	100	100	110	90	100
DE 83R					15		50			80	70	100
BUSAN 11-M1	37	37	37	37	20	20	10	25	25	20	15	20
Calcium Oxide					20	10	5	20	20	10	20	15
MONARCH 280	7	7	7	7	10	5	10	5	5	10	10	10
ULTRA PFLEX	300	300	300	300	180	300	80	213	213	127	146	158
DYHARD UR 300	7	7	7	7	6	10	4	10	10	20	16	16
EXPANCEL 551	8.4	8.4	8.4	8.4	8.8	9.5	7.8	13.4	13.4	18.8	19.1	17.8
Cab-O-Sil TS 720	41	41	41	41	30	32	34	64	64	66	65	62
EPODIL 749	37	37	37	37	15	20	10	40	40	20	50	50

Component / Adhesive	37	38	39	40	41	42	43	44	45	46	47	48
SF-65 A (Example 1)												778
SF-65 B (Example 1)							230					
SF-65 C (Example 1)												
SF-65 D (Example 1)	865											
SF-65 E (Example 1)									500	500		
SF-65 F (Example 1)						190					314	
SF-65 G (Example 1)												
SF-65 H (Example 1)					480							
SF-65 J (Example 1)								271				
Polydis 3604		225	300	380	106	80	50		90	90		
EPON 828		615	800	800	106	150	200	388	600	600	300	250
EPON 834						60			120	120	54	100
DER 351	300					60						
DER 354		135						33			50	200
Resin A (Example 2)												
Resin B (Example 2)												
Resin C (Example 2)		150			89							
Resin D (Example 2)												
Resin E (Example 2)												
Resin F (Example 2)												
Resin G (Example 2)						130						
Resin H (Example 2)												
Resin J (Example 2)												
Resin K (Example 2)												
Resin L (Example 2)												
Resin M (Example 2)			260							200		130
Resin N (Example 2)	280			380			80	50	200		50	
AMICURE CG 1400	100	106	128	140	65	55	50	57	100	100	55	90
DE 83R	100	60	100			15		50			40	70
BUSAN 11-M1	20	15	30	40	37	20	20	10	25	25	10	15
Calcium Oxide	15	15	10			20	10	5	20	20	29	20
MONARCH 280	10	8	10	10	7	10	5	10	5	5	5	10
ULTRA PFLEX	158	150	260	100	300	180	300	80	213	213	50	146
DYHARD UR 300	16	8	14	60	7	6	10	4	10	10	10	16
EXPANCEL 551	17.8	8.0	14.2	13.8								
Cab-O-Sil TS 720	62	49	72	72	41	30	32	34	64	64	33	65
EPODIL 749	50				37	15	20	10	40	40		50

Component / Adhesive	49	50	51	52
SF-65 A (Example 1)				
SF-65 B (Example 1)				
SF-65 C (Example 1)				
SF-65 D (Example 1)	865			
SF-65 E (Example 1)				
SF-65 F (Example 1)				
SF-65 G (Example 1)				
SF-65 H (Example 1)				
SF-65 J (Example 1)				
Polydis 3604		225	300	380
EPON 828		615	800	800
EPON 834				
DER 351	300			
DER 354		135		
Resin A (Example 2)				
Resin B (Example 2)				
Resin C (Example 2)		150		
Resin D (Example 2)				
Resin E (Example 2)				
Resin F (Example 2)				
Resin G (Example 2)				
Resin H (Example 2)				
Resin J (Example 2)				
Resin K (Example 2)				
Resin L (Example 2)				
Resin M (Example 2)	280		260	
Resin N (Example 2)				380
AMICURE CG 1400	100	106	128	140
DE 83R	100	60	100	
BUSAN 11-M1	20	15	30	40
Calcium Oxide	15	15	10	
MONARCH 280	10	8	10	10
ULTRA PFLEX	158	150	260	100
DYHARD UR 300	16	8	14	60
EXPANCEL 551				
Cab-O-Sil TS 720	62	49	72	72
EPODIL 749	50			

**TABLE 2**

Component	Chemical name of component	Tradename of Company
SF-65	Epoxy-Based Prepolymer	
Polydis 3604	CTBN-Epoxy adduct	Struktol
EPON 828	diglycidylether of bisphenol A	Resolution Performance Products
EPON 834	diglycidylether of bisphenol A	Resolution Performance Products
DER 351	diglycidylether of bisphenol A and F	Dow Chemical
DER 354	diglycidylether of bisphenol F	Dow Chemical
Resin A-N (Example 2)	acrylate terminated urethane resin	
AMICURE CG 1400	Dicyandiamide	Air Products
DE 83R	decabromodiphenyl ether	Great Lakes Chemical Corp
BUSAN 11-M1	Barium metaborate monohydrate	Buckman Laboratories
Calcium Oxide	Calcium Oxide	
MONARCH 280	carbon black	Cabot
ULTRA PFLEX	coated precipitated calcium carbonate	Pfizer
DYHARD UR 300	Fenuron	SKW Trostberg
EXPANCEL 551	Poly(acrylonitrile-co-vinylidene chloride) shell, with isobutene encapsulated therein	Akzo Nobel
Cab-O-Sil TS 720	treated fumed silica	Cabot
Epodil 749	Neopentyl glycol diglycidyl ether	Air Products

5 Curing: Fix bond with clips and place specimens for 20 min in an air-circulating oven at 160C.

Table 3 below describes the properties of the above described adhesives following curing.

**TABLE 3**  
**PROPERTIES**

Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
1	110sec/20gms @32.1C	AVE.= 97 %	EZG: AVE.= 13.8 MPa	EZG: 151 N/25mm
	25.8sec/20gms @39.0C		HDG: AVE.= 13.0 MPa	HDG: 133 N/25mm
2	138sec/20gms @33.3C	AVE.= 89 %	EZG: AVE.= 9.1 MPa	EZG: 107 N/25mm
	31.4sec/20gms @40.1C		HDG: AVE.= 6.6 MPa	HDG: 94 N/25mm
3	98.2sec/20gms @32.4C	AVE.= 99 %	EZG: AVE.= 13.6 MPa	EZG: 150 N/25mm
	20.8sec/20gms @38.4C		HDG: AVE.= 13.3 MPa	HDG: 138 N/25mm
4	107sec/20gms @32.0C	AVE.= 90 %	EZG: AVE.= 11.4 MPa	EZG: 153 N/25mm
	23.8sec/20gms @38.9C		HDG: AVE.= 10.0 MPa	HDG: 129 N/25mm
5	110sec/20gms @31.8	AVE.= 103 %	EZG: AVE.= 12.5 MPa	EZG: 147 N/25mm
	20.0sec/20gms @39.5C		HDG: AVE.= 12.1 MPa	HDG: 130 N/25mm
6	59.9sec/20gms @32.0C	AVE.= 118 %	EZG: AVE.= 13.5 MPa	EZG: 139 N/25mm
	14.5sec/20gms @39.3C		HDG: AVE.= 12.1 MPa	HDG: 125 N/25mm
7	23.7sec/20gms @32.2C	AVE.= 79 %	EZG: AVE.= 15.1 MPa	EZG: 126 N/25mm
	7.3sec/20gms @39.5C		HDG: AVE.= 14.2 MPa	HDG: 112 N/25mm
8	10.1sec/20gms @32.5	AVE.= 47 %	EZG: AVE.= 18.6 MPa	EZG: 107 N/25mm
	5.9sec/20gms @39.8C		HDG: AVE.= 12.7 MPa	HDG: 87 N/25mm
9	28.0sec/20gms @32.0C	AVE.= 81 %	EZG: AVE.= 15.6 MPa	EZG: 118 N/25mm

Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
	9.4sec/20gms @39.1C		HDG: AVE.= 14.9 MPa	HDG: 102 N/25mm
10	100sec/20gms @32.2C	AVE.= 99 %	EZG: AVE.= 14.4 MPa	EZG: 140 N/25mm
	23.7sec/20gms @39.0C		HDG: AVE.= 13.8 MPa	HDG: 123 N/25mm
11	144sec/20gms @30.9C	AVE.= 106 %	EZG: AVE.= 11.9 MPa	EZG: 135 N/25mm
	26.1sec/20gms @40.2C		HDG: AVE.= 11.2 MPa	HDG: 122 N/25mm
12	138sec/20gms @31.5C	AVE.= 96 %	EZG: AVE.= 14.1 MPa	EZG: 156 N/25mm
	25.8sec/20gms @39.0C		HDG: AVE.= 13.5 MPa	HDG: 144 N/25mm
13	115sec/20gms @31.9C	AVE.= 99 %	EZG: AVE.= 13.8 MPa	EZG: 150 N/25mm
	29.8sec/20gms @38.1C		HDG: AVE.= 12.7 MPa	HDG: 135 N/25mm
14	96.0sec/20gms @31.3C	AVE.= 87 %	EZG: AVE.= 8.1 MPa	EZG: 72 N/25mm
	20.8sec/20gms @39.1C		HDG: AVE.= 8.3 MPa	HDG: 72 N/25mm
15	101.6sec/20gms @31.5C	AVE.= 92 %	EZG: AVE.= 4.5 MPa	EZG: 58 N/25mm
	23.0sec/20gms @39.0C		HDG: AVE.= 4.8 MPa	HDG: 53 N/25mm
16	95.6sec/20gms @32.3C	AVE.= 101 %	EZG: AVE.= 16.8 MPa	EZG: 166 N/25mm
	25.8sec/20gms @39.0C		HDG: AVE.= 14.3 MPa	HDG: 131 N/25mm
17	91.1sec/20gms @32.3C	AVE.= 108 %	EZG: AVE.= 14.6 MPa	EZG: 170 N/25mm
	25.4sec/20gms @37.8C		HDG: AVE.= 13.0 MPa	HDG: 143 N/25mm
18	101sec/20gms @32.2C	AVE.= 92 %	EZG: AVE.= 13.0 MPa	EZG: 150 N/25mm



Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
	25.4sec/20gms @38.8C		HDG: AVE.= 13.0 MPa	HDG: 139 N/25mm
19	106sec/20gms @32.3C	AVE.= 95 %	EZG: AVE.= 13.5 MPa	EZG: 148 N/25mm
	28.1sec/20gms @38.5C		HDG: AVE.= 13.2 MPa	HDG: 135 N/25mm
20	136sec/20gms @32.4C	AVE.= 109 %	EZG: AVE.= 15.2 MPa	EZG: 168 N/25mm
	36.8sec/20gms @38.8C		HDG: AVE.= 14.5 MPa	HDG: 157 N/25mm
21	102sec/20gms @32.4C	AVE.= 97 %	EZG: AVE.= 13.8 MPa	EZG: 148 N/25mm
	22.0sec/20gms @40.0C		HDG: AVE.= 12.9 MPa	HDG: 135 N/25mm
22	220sec/20gms @32.4C	AVE.= 112 %	EZG: AVE.= 16.9 MPa	EZG: 131 N/25mm
	40.1sec/20gms @38.6C		HDG: AVE.= 15.4 MPa	HDG: 133 N/25mm
23	184sec/20gms @32.3C	AVE.= 116 %	EZG: AVE.= 15.7 MPa	EZG: 129 N/25mm
	31.8sec/20gms @38.4C		HDG: AVE.= 14.9 MPa	HDG: 124 N/25mm
24	18.1sec/20gms @32.3	AVE.= 116 %	EZG: AVE.= 17.6 MPa	EZG: 118 N/25mm
	8.7sec/20gms @39.8C		HDG: AVE.= 14.3 MPa	HDG: 111 N/25mm
25	198sec/20gms @32.0C	AVE.= 90 %	EZG: AVE.= 16.6 MPa	EZG: 125 N/25mm
	40.0sec/20gms @38.3C		HDG: AVE.= 15.3 MPa	HDG: 125 N/25mm
26	14.3sec/20gms @33.0	AVE.= 107 %	EZG: AVE.= 17.8 MPa	EZG: 120 N/25mm
	8.8sec/20gms @39.2C		HDG: AVE.= 15.0 MPa	HDG: 122 N/25mm
27	214sec/20gms @32.5C	AVE.= 92 %	EZG: AVE.= 15.4 MPa	EZG: 133 N/25mm

Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
	40.8sec/20gms @38. C		HDG: AVE.= 14.0 MPa	HDG: 127 N/25mm
28	15.5sec/20gms @32.6	AVE.= 102 %	EZG: AVE.= 17.0 MPa	EZG: 109 N/25mm
	9.5sec/20gms @38.8C		HDG: AVE.= 14.6 MPa	HDG: 98 N/25mm
29	71.8sec/20gms @32.1C	AVE.= 98 %	EZG: AVE.= 16.8 MPa	EZG: 129 N/25mm
	23.8sec/20gms @39.2C		HDG: AVE.= 15.6 MPa	HDG: 128 N/25mm
30	67.6sec/20gms @31.9C	AVE.= 107 %	EZG: AVE.= 16.5 MPa	EZG: 130 N/25mm
	23.3sec/20gms @39.0C		HDG: AVE.= 15.5 MPa	HDG: 126 N/25mm
31	82.4sec/20gms @32.0C	AVE.= 103 %	EZG: AVE.= 16.9 MPa	EZG: 125 N/25mm
	27.5sec/20gms @39.2C		HDG: AVE.= 15.7 MPa	HDG: 127 N/25mm
32	70.5sec/20gms @31.8C	AVE.= 96 %	EZG: AVE.= 16.7 MPa	EZG: 132 N/25mm
	20.9sec/20gms @39.2C		HDG: AVE.= 15.5 MPa	HDG: 120 N/25mm
33	90.2sec/20gms @31.9C	AVE.= 92 %	EZG: AVE.= 17.3 MPa	EZG: 138 N/25mm
	24.7sec/20gms @39.1C		HDG: AVE.= 15.9 MPa	HDG: 128 N/25mm
34	74.4sec/20gms @32.0C	AVE.= 106 %	EZG: AVE.= 16.7 MPa	EZG: 130 N/25mm
	17.4sec/20gms @39.3C		HDG: AVE.= 15.2 MPa	HDG: 127 N/25mm
35	76.1sec/20gms @32.0C	AVE.= 103 %	EZG: AVE.= 14.7 MPa	EZG: 150 N/25mm
	19.0sec/20gms @39.4C		HDG: AVE.= 14.3 MPa	HDG: 139 N/25mm
36	71.0sec/20gms @31.8C	AVE.= 100 %	EZG: AVE.= 15.9 MPa	EZG: 132 N/25mm

Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
	15.5sec/20gms @39.3C		HDG: AVE.= 14.8 MPa	HDG: 129 N/25mm
37	65.9sec/20gms @32.2C	AVE.= 105 %	EZG: AVE.= 16.1 MPa	EZG: 130 N/25mm
	14.1sec/20gms @39.0C		HDG: AVE.= 15.5 MPa	HDG: 130 N/25mm
38	14.2sec/20gms @32.0C	AVE.= 117 %	EZG: AVE.= 16.6 MPa	EZG: 100 N/25mm
	4.3sec/20gms @39.1C		HDG: AVE.= 15.5 MPa	HDG: 94 N/25mm
39	16.2sec/20gms @31.8C	AVE.= 121 %	EZG: AVE.= 16.9 MPa	EZG: 113 N/25mm
	6.6sec/20gms @39.0C		HDG: AVE.= 15.4 MPa	HDG: 102 N/25mm
40	12.9sec/20gms @31.9C	AVE.= 106 %	EZG: AVE.= 15.7 MPa	EZG: 130 N/25mm
	4.0sec/20gms @38.7C		HDG: AVE.= 15.0 MPa	HDG: 121 N/25mm
41	16.1sec/20gms @32.2		EZG: AVE.= 26.3 MPa	EZG: 186 N/25mm
	9.1sec/20gms @39.0C		HDG: AVE.= 18.9 MPa	HDG: 164 N/25mm
42	70.0sec/20gms @32.3C		EZG: AVE.= 27.0 MPa	EZG: 201 N/25mm
	23.5sec/20gms @39.0C		HDG: AVE.= 21.9 MPa	HDG: 172 N/25mm
43	67.0sec/20gms @32.09C		EZG: AVE.= 26.9 MPa	EZG: 190 N/25mm
	24.7sec/20gms @38.8C		HDG: AVE.= 22.2 MPa	HDG: 166 N/25mm
44	80.1sec/20gms @32.0C		EZG: AVE.= 27.1 MPa	EZG: 196 N/25mm
	31.9sec/20gms @39.0C		HDG: AVE.= 20.4 MPa	HDG: 167 N/25mm
45	65.2sec/20gms @31.9C		EZG: AVE.= 25.7 MPa	EZG: 202 N/25mm

Adhesive #	Viscosity (Flow at 80psi, 0.104inch)	Expansion@ 160C/20min.	Shear Strength w/oil 160C for 20 min.	T-Peel Strength w/oil 160C for 20 min.
	19.7sec/20gms @39.0C		HDG: AVE.= 20.5 MPa	HDG: 160 N/25mm
46	100.1sec/20gms @31.8C		EZG: AVE.= 26.6 MPa	EZG: 196 N/25mm
	28.1sec/20gms @38.7C		HDG: AVE.= 21.5 MPa	
47	150.0sec/20gms @35.0C		EZG: AVE.= 25.1 MPa	EZG: 191 N/25mm
	76.8sec/20gms @39.2C		HDG: AVE.= 19.4 MPa	HDG: 168 N/25mm
48	42.6sec/20gms @35.0C		EZG: AVE.= 24.3 MPa	EZG: 203 N/25mm
	19.5sec/20gms @39.2C		HDG: AVE.= 19.0MPa	
49	37.2sec/20gms @35.1C		EZG: AVE.= 24.7 MPa	EZG: 223 N/25mm
	15.5sec/20gms @39.3C		HDG: AVE.= 19.3 MPa	
50	9.0sec/20gms @34.9C		EZG: AVE.= 28.0 MPa	EZG: 167 N/25mm
	4.5sec/20gms @39.0C		HDG: AVE.= 20.9 MPa	
51	13.4sec/20gms @35.1C		EZG: AVE.= 27.6 MPa	EZG: 188 N/25mm
	6.2sec/20gms @38.9C		HDG: AVE.= 22.7 MPa	
52	10.0sec/20gms @32.0C		EZG: AVE.= 25.6 MPa	EZG: 214 N/25mm
	4.0sec/20gms @38.7C		HDG: AVE.= 21.8 MPa	

## WHAT IS CLAIMED IS:

1. A curable adhesive comprising:
  - 5 A) an epoxy-based prepolymer comprising the reaction product of  
(a) an epoxy resin; and  
(b) a co-reactant selected from the group consisting of amino-terminated polyethers, carboxyl-containing 1,3-diene/polar ethylenically unsaturated comonomer resins, and mixtures thereof;
  - 10 B) an acrylate-terminated urethane resin comprising the reaction product of a polyfunctional isocyanate, a polyol having a number average molecular weight of at least about 400, and an isocyanate reactive (meth)acrylate; and
  - C) a heat-activated latent curing agent.
- 15 2. The curable adhesive of claim 1 which additionally comprises an expanding agent.
3. The curable adhesive of claim 2 wherein the expanding agent comprises expandable hollow plastic microspheres.
- 20 4. The curable adhesive of claim 1 in which the acrylate-terminated urethane resin is produced by reacting the polyfunctional isocyanate and the polyol to form an isocyanate terminated urethane prepolymer and then reacting the isocyanate reactive (meth)acrylate with the isocyanate terminated urethane prepolymer.
- 25 5. The curable adhesive of claim 1 in which the polyol is selected from the group consisting of polypropylene polyols, polyester polyols, polycaprolactone polyols, polytetrahydrofuran polyols, and mixtures thereof.
- 30 6. The curable adhesive of claim 1 in which the polyfunctional isocyanate is an aromatic diisocyanate.
7. The curable adhesive of claim 1 in which the number average molecular weight of the polyol is from about 400 to about 4000.

8. The curable adhesive of claim 1 in which the epoxy resin is selected from the group consisting of diglycidyl ethers of bisphenol A and bisphenol F.
9. The curable adhesive of claim 1 in which the polyol is selected from the group consisting of polypropylene glycols, polyester polyols, polytetramethylene glycols, and mixtures thereof and the polyfunctional isocyanate is selected from the group consisting of 2,4-toluenediisocyanate, 2,6-toluenediisocyanate, methylenediphenyldiisocyanate, isophoronediiisocyanate, hexamethylenediisocyanate, paraphenylenediisocyanate and mixtures thereof.
10. The curable adhesive of claim 1 in which the isocyanate reactive acrylates and methacrylates are selected from the group consisting of hydroxyalkyl acrylates, hydroxyalkyl methacrylates, and mixtures thereof.
11. The curable adhesive of claim 1 wherein at least a portion of the epoxy-based prepolymer comprises the reaction product of a diglycidyl ether of bisphenol A or bisphenol F and a carboxyl-terminated butadiene-nitrile rubber.
12. The curable adhesive of claim 1 which comprises at least one substituted guanidine heat-activated latent curing agent.
13. A curable adhesive comprising:
- A) an epoxy-based prepolymer which comprises the reaction product of
    - a. a first epoxy resin which is solid at room temperature and which is a diglycidyl ether of bisphenol A or bisphenol F, having an epoxide equivalent weight of from about 400 to about 700;
    - b. a second epoxy resin which is liquid at room temperature and which is a diglycidyl ether bisphenol A or bisphenol F, having an epoxide equivalent weight of from about 150 to about 220; and
    - c. an amino-terminated polyalkylene glycol selected from the group consisting of polyethylene and polypropylene glycols;
  - B) an acrylate terminated urethane resin which comprises the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive acrylate or methacrylate, wherein the isocyanate terminated urethane prepolymer is obtained by reaction of a polyol

having a number average molecular weight of at least about 400 and a polyfunctional isocyanate;

- C) a heat-activated latent curing agent; and
- D) an expanding agent comprising hollow plastic microspheres.

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14. A curable adhesive which comprises:

- A) a reaction product of a polyepoxide resin having at least two 1,2-epoxy groups per molecule with an amino-terminated polyalkylene glycol and, optionally, an epoxy adduct of a carboxyl-terminated butadiene-nitrile rubber;
- B) an acrylate-terminated urethane resin which comprises the reaction product of an isocyanate terminated urethane prepolymer and an isocyanate reactive (meth)acrylate, wherein the isocyanate terminated urethane prepolymer is obtained by reaction of a polyol having a number average molecular weight of at least about 400 and a polyfunctional isocyanate; and
- C) a heat-activated latent curing agent.

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15. A curable adhesive which comprises:

- A) an epoxy-based prepolymer comprising the reaction product of
  - a. a first epoxy resin which is solid at room temperature and which is a diglycidyl ether of bisphenol A or bisphenol F, having an epoxide equivalent weight of from about 400 to about 700;
  - b. a second epoxy resin which is liquid at room temperature and which is a diglycidyl ether of bisphenol A or bisphenol F, having an epoxide equivalent weight of from about 150 to about 220; and
  - c. a co-reactant selected from the group consisting of amino-terminated polyalkylene glycols, carboxyl-terminated butadiene-nitrile resins, and mixtures thereof;
- B) an acrylate-terminated urethane resin;
- C) a heat-activated latent curing agent; and
- D) an expanding agent comprising hollow microspheres.

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16. A method of making a composite article which comprises: contacting a surface with the curable adhesive of claim 1 and curing the curable adhesive in contact with the surface to prepare a composite article.
- 5 17. The method of claim 16 in which the surface is metal or plastic.
18. The method of claim 16 in which at least two surfaces are contacted with the curable adhesive and cured in contact therewith.
- 10 19. The method of claim 16 in which the curable adhesive is flowed into contact with the surface at a temperature between about 10 and 50 degrees C.
20. The method of claim 16 in which the curable adhesive is flowed into contact with the surface at a temperature of about 20 and about 40 degrees C.
- 15 21. The method of claim 16 in which the curable adhesive contains expandable hollow plastic microspheres.
- 20



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/07942

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC(7) : B32B 27/38; C08J 09/32		
US CL : 428/413, 414, 416, 418; 521/134, 138; 523/218, 400, 427, 500, 538; 525/107, 109; 528/103, 124		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
U.S. : 428/413, 414, 416, 418; 521/134, 138; 523/218, 400, 427, 500, 538; 525/107, 109; 528/103, 124		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,891,367 A (BASHEER et al.) 6 April 1999 (06.04.1999), col.3, line 35-col.4, line 20, col.7, lines 1-25, col.13, lines 7-16, and Figures 1 and 2.	1,4-10,14,16-20
X	US 5,198,524 A (BUSH et al.) 30 March 1993 (30.03.1993), col.9, Example 6, col.4, lines 9-25, and col.6, lines 10-30.	14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
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Name and mailing address of the ISA/US		Authorized officer
Mail Stop PCT, Attn: ISA/US		Robert A. Dawson
Commissioner for Patents		Telephone No. (703) 308-0661
P.O. Box 1450		
Alexandria, Virginia 22313-1450		
Facsimile No. (703)305-3230		

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